(54) Title: FAST CURING EPOXY RESINS AND A PROCESS FOR THEIR PREPARATION

(57) Abstract

Epoxy resins containing both terminal hydroxyl groups and epoxy-derived groups are prepared by advancing a polyepoxide with a polyol and terminating the reaction at a point such that the epoxy resin reaction product contains both epoxy and terminal hydroxyl groups. The epoxy groups are then further reacted to form epoxy-derived groups and the rate of curing is further improved. The resulting epoxy resins exhibit lower melt and solution viscosities than those exhibited by conventional epoxy resins having the same epoxy equivalent weight, as well as curing quickly when used. The resins are usefully employed at high solids levels in can coating formulations and other epoxy formulations wherein the resin is applied from an organic liquid solution or aqueous dispersion.
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FAST CURING EPOXY RESINS
AND A PROCESS FOR THEIR PREPARATION

The present invention relates to epoxy resins; to a process for preparing said resins and to compositions containing these resins.

Due to their physical and chemical properties such as resistance to chemical attack, good adhesion to various substrates, solvent resistance and hardness, epoxy resins are useful in a wide variety of commercial applications including the coating of various substrates such as metal, wood and plastic, and the preparation of structural and electrical laminates. In many applications such as the coating of the interior of containers ("cans"), the epoxy resin is applied from an organic liquid solution or aqueous dispersions.

Epoxy resins of differing molecular weight (so-called 'advanced epoxy resins") can be prepared by the reaction of a polyepoxide such as the diglycidyl ether of bisphenol A with a polyhydric phenol such as bisphenol A.

The molecular weight of the epoxy resin generally affects the softening point, melt viscosity and
solution viscosity of the epoxy resin as well as the physical and chemical properties of the cured product prepared therefrom. It is often desirable to prepare as high a molecular weight epoxy resin as practical to provide a product of sufficient toughness. High molecular weight resins are generally prepared by a two-step process wherein a lower molecular weight epoxy resin is prepared initially by reacting a polyhydric phenol with epichlorohydrin and alkali metal hydroxide in the presence of a catalyst. Thereafter, the initial polyepoxide reaction product is advanced by its reaction with additional amounts of polyhydric phenol to form the higher molecular weight material. In conventional techniques for preparing the epoxy resins, the reaction of the polyepoxide and polyhydric phenol is typically carried to complete conversion such that the final, advanced epoxy resin contains relatively low amounts of residual phenolic hydroxyl groups. For example, epoxy resins having an EEW (epoxy equivalent weight) between 500 and 700 prepared from bisphenol A and the diglycidyl ether of bisphenol A typically contain less than 800 parts per million of phenolic hydroxyl groups which represents more than about 98 percent conversion of the phenolic hydroxyl groups employed in preparing the epoxy resin. A higher molecular weight epoxy resin having an EEW from greater than about 2000 to about 4000 typically contains less than about 2500 ppm of phenolic OH groups which represents more than about 95 percent conversion of the phenolic hydroxyl groups. Any residual hydroxyl groups in the advanced resin have been stated to cause viscosity instability of the resulting resin mixture, particularly at elevated temperatures. As a means for controlling the stability of the resin due to the
unreacted phenolic hydroxyl groups, U.S. Patent No. 3,842,037 suggests adding a strong, inorganic acid when at least about 85, more preferably at least about 95, percent of the phenolic hydroxyl groups employed in the advancement reaction have been reacted.

Alternatively, in another method for preparing a high molecular weight epoxy resin, U.S. Patent No. 3,352,825 teaches condensing a dihydric phenol with an excess of epichlorohydrin in the presence of a catalyst such as an alkali metal or ammonium salt of an inorganic monobasic acid to form an intermediate having a free hydroxyl content in the range of from 0.2 to 0.95 phenolic hydroxyl group per mole of said dihydric phenol. Subsequently, the excess epichlorohydrin is removed and the intermediate condensate subsequently dehydrochlorinated, using caustic alkali and simultaneously the free phenolic hydroxyl groups are reacted with the epoxy groups formed in situ to form a product free of hydroxy groups.

Unfortunately, increasing the molecular weight of an epoxy resin also generally increases the melt and solution viscosities of the resin. Such increase in melt and solution viscosities renders the application of the epoxy resin more difficult.

One method by which the melt and solution viscosities of an epoxy resin can be reduced for a given EEW is by regulating the chain growth using a monofunctional reactant such as a monofunctional phenolic or epoxy compound as a capping agent. Unfortunately, the use of these capping agents results in a formation of an epoxy resin having reduced epoxy functionality and a lower softening point at a given
EEW. The reduction in epoxy functionality markedly reduced the physical properties such as toughness of the cured resin product prepared therefrom.

In European patent application EP 85 00416 there is disclosed an epoxy resin comprising the reaction product of a polyepoxide and a polyol wherein the reaction product contains both epoxy groups and terminal hydroxyl groups in an amount of at least about 0.25 weight percent of each of the epoxy groups and the terminal hydroxyl groups, said weight percent being based on the total weight of the epoxy resin reaction product. The epoxy resins of that application, which are hereinafter referred to as Controlled Conversion Resins (CCR resins), offer a significant number of advantages over conventional epoxy resins which are fully converted and contain essentially no terminal hydroxyl groups. For example, the melt and solution viscosity of the CCR resins are reduced when compared to conventional epoxy resins having the same EEW. Moreover, the epoxy resins of that application are capable of being cured to chemically resistant products having physical properties which are essentially equivalent to conventional resins.

Due to the fact that CCR resins of European patent application EP 85 00416 contain both epoxy and terminal hydroxyl groups, the CCR resins can constitute a convenient homogeneous, one-component system which need not require an additional hardener.

Due to the lower solution viscosity of the CCR resins, the resins are capable of being formulated in an organic liquid at a higher solids level than conventional epoxy resins having the same EEW to
prepare solutions having equivalent viscosities. Such high solid epoxy resin formulations can be conveniently applied to a substrate to form a coating of equivalent flexibility and chemical resistance at a coating prepared from a conventional epoxy resin applied from a solution of lower solids content. It was found, however, that according to the present invention such CCR resins, while suitable for producing very desirable resin products and coatings could have their curing times improved even more while maintaining the excellent product properties when the epoxy groups were further reacted.

According to the present invention, controlled conversion resins are produced, suitable for use at high solids content having improved curing times as well as excellent stability during storage and/or prior to use. Accordingly, in one aspect the present invention is an epoxy resin comprising the reaction product of a polyepoxide and a polyol wherein the reaction product contains both (a) terminal phenolic hydroxyl groups in an amount of at least 0.15 equivalent per kilogram resin (eq/kg) and (b) groups derived from epoxy groups and optionally epoxy groups in a total amount which is greater than 0.05 equivalents per kilogram resin. The method for the calculation of eq/kg as used herein is described below in connection with Table 1.

In another aspect, the present invention is a process for preparing an epoxy resin which method comprises reacting a polyepoxide with a polyol in the presence of a catalyst for the reaction of an epoxy group with a hydroxyl group and terminating the reaction at a point when the reaction product contains
at least 0.05 equivalents epoxy groups per kilogram resin and 0.15 equivalents terminal phenolic hydroxyl groups per kilogram resin, then reacting at least a portion of the epoxy groups to form epoxy-derived groups. The epoxy resins according to the present invention are found to surprisingly possess all the advantageous properties of controlled conversion resins with the additional, unexpected benefit of improved curing times combined with excellent stability. It is especially preferred to convert at least a portion of the epoxy groups on these CCR resins, to phosphate ester groups and alpha glycols.

The polyol component advantageously employed in preparing the CCR resin is a polyhydric alcohol containing an average of more than about one hydroxyl group, preferably about 1.8 or more hydroxyl groups, reactive with the epoxy groups of the polyepoxide. The polyols can be saturated or unsaturated aliphatic, cycloaliphatic, aromatic or heterocyclic compounds which can be substituted with one or more non-interfering substituents such as halogen atoms or ether radicals. In general, the preferred polyols are polyhydric phenols. The polyhydric phenols advantageously employed in preparing the epoxy resins are polyhydric phenols represented by the following structural formula
Wherein each A is independently $\text{-O-; \ -S-, \ -S-S-, \ -C(O)-, \ -S(O)-, \ -S(O)_{2}-}$, a divalent hydrocarbon radical containing from about 1 to about 8 carbon atoms, or a divalent oxygen, sulfur, or nitrogen-containing hydrocarbon radical or a covalent bond; each X is independently hydrogen, halogen, or an alkyl group containing from about 1 to 4 carbon atoms and n has an average value of from 0 to about 5, preferably from 0 to about 2; and the novolac resins (phenol-aldehyde) condensates of the formula:

wherein each R is individually hydrogen or an alkyl radical having from about 1 to about 4 carbon atoms, each Y is independently hydrogen, chlorine, bromine or a lower alkyl group and m has an average value from 0
to about 10. Mixtures of one or more polyhydric phenols are also suitably employed herein.

Preferably, the polyhydric phenol is a polyhydric phenolic compound of the general structural formula (I) wherein A is a divalent hydrocarbon radical having from 1 to about 8 carbon atoms, each X is hydrogen, and n has an average value of from 0 to about 0.5, more preferably 0. Most preferred of the polyhydric phenols is 2,2-bis(-4-hydroxy phenyl) propane, commonly referred to as bisphenol A (BPA).

The polyepoxide component useful in preparing the epoxy resin of the present invention is a compound having two or more epoxide groups. The polyepoxides can be saturated or unsaturated aliphatic, cycloaliphatic, aromatic or heterocyclic compounds and can be substituted with one or more non-interfering substituents such as halogen atoms or ether radicals which are not reactive with the epoxy or hydroxyl groups at the conditions at which the CCR resins are prepared. The polyepoxide component which is reacted with the polyol to form the CCR resin can be monomeric or polymeric.

Illustrative examples of epoxy resins useful herein are described in The Handbook of Epoxy Resins by H. Lee and K. Neville, published in 1967 by McGraw-Hill, New York, in appendix 4-1, ppgs. 4-35 through 4-56.

Polyepoxides of particular interest in the practice of this embodiment include the polyglycidyl ethers of bisphenol compounds represented by the general structural formula:
wherein each A and X are as described above in the description of formula (I) and n has an average value of 0 to 4, preferably 0 to 2, most preferably from 0 to 0.5; the polyglycidyl ethers of a novolac resin, i.e., phenol aldehyde condates of the formula

wherein R, Y and m are described as above with reference to formula (II); polyglycidyl ethers of polyglycols such as the diglycidyl ether of polypropylene glycol; and the polyglycidyl ethers of tris(phenol)methane. Mixtures of one or more polyepoxides are also suitably employed herein. Preferred polyepoxides are the liquid polyglycidyl polyethers of a bisphenol, particularly the diglycidylethers of bisphenol A; the polyglycidyl polyethers of a tetrabromobisphenol, particularly the
diglycidylether of tetrabromobisphenol A and mixtures thereof.

The polyepoxide and polyol are advantageously employed in an amount such that the number of epoxy equivalents in the polyepoxide to the number of hydroxyl equivalent of the polyol is from 0.1:1 to 10:1. Preferably, the polyepoxide and polyol components are employed in a ratio from 0.3:1 to 5:1, more preferably from 0.3:1 to 2:1, epoxy equivalents to hydroxyl equivalents. The reactive proportions of the polyepoxide and polyol components most advantageously employed will be dependent on a variety of factors including the specific polyepoxide and polyol employed and the desired properties of the epoxy resin prepared therefrom. In a preferred CCR resin, the polyepoxide component is employed in less than a stoichiometric amount. In a most preferred embodiment, from about 0.6:1 to about 1.6:1 hydroxyl equivalents are employed for each epoxy equivalent of the polyepoxide.

In preparing the CCR resins, the polyol and the polyepoxide components are contacted in the presence of a catalyst for the reaction between the hydroxyl groups of the polyol and the epoxy groups of the polyepoxide and at conditions sufficient to form the desired CCR resin. Preferably, this reaction is conducted neat, i.e., in the absence of any reaction diluent.

Materials capable of catalyzing the stated reaction are well-known in the art and reference is made thereto for the purposes of this invention. Illustrative catalysts are set forth in U.S. Patent Nos. 2,216,099; 2,633,458; 2,658,855; 3,377,406; 3,694,407; 3,948,855; 4,389,520; 4,354,015; and
3,477,990 and *The Handbook of Epoxy Resins* by H. Lee and K. Neville, published in 1967 by McGraw-Hill, New York, all of which are incorporated herein by reference. Representative of the described catalysts are secondary and tertiary amines, preferably tertiary amines such as benzyl dimethyl amine, triethyl amine and benzyl diethyl amine; the alkali metal hydroxides e.g., potassium hydroxide; quaternary ammonium compounds such as tetralkylammonium halides, e.g., tetramethyl ammonium chloride and phosphines and quaternary phosphonium salts such as triphenyl phosphine and ethyltriphenyl phosphonium acetate-acetic acid complex.

The catalyst is typically employed in conventional amounts. These amounts will vary depending on the specific catalyst, polyepoxide and polyol employed but will preferably vary from about 0.005 to about 1 weight percent based on the total weight of the polyol and polyglycidyl ether components. More preferably, from about 0.01 to about 0.5 weight percent of the catalyst is employed, said weight percent being based on the total weight of the polyol and polyepoxide components.

Although not preferred, the reaction of the polyol and polyepoxide components can be conducted in the presence of a reaction diluent. If employed, the reaction diluent is preferably a solvent for a miscible with both the polyol and polyepoxide component. Representative solvents which can be employed include various glycol ethers such as ethylene or propylene glycol monomethylether and esters thereof such as ethylene glycol monoethylether acetate; ketones such as methylisobutylketone, methylethylketone and acetone;
and aromatic hydrocarbons such as toluene, xylene or mixtures thereof. If employed, the organic liquid reaction diluent is generally employed in an amount from about 5 to about 300 percent based on the total weight of the polyl and polyepoxide components.

The reaction of the polyl and polyepoxide is advantageously carried out at an elevated temperature, preferably from about 60°C to about 200°C, more preferably from about 100°C to about 180°C. The reaction is continued until the desired conversion as determined by measuring the residual epoxy and terminal hydroxyl content in the resin, at which point, the reaction is effectively terminated.

As described in European Patent Application EP 85 00416, the CCR resins are prepared using any method which effectively inhibits the reaction upon reaching the desired degree of conversion. The reaction is effectively inhibited when the rate of reaction of the hydroxyl and epoxy group is sufficiently reduced such that further reaction, if any, does not significantly and deleteriously affect the product or its handling characteristics. Preferably, the reaction is sufficiently inhibited such that the solution viscosity of the CCR resin remains essentially constant or increases only marginally with time. For example, upon reaching the desired degree of conversion the reaction mixture can be quenched to stop the reaction. However, the rapid quenching of the reaction mixture must be conducted carefully to prevent clotting or lumping of the CCR resin and to prevent the CCR resin from forming a large solid mass which cannot subsequently be used.
A convenient method for cooling the reaction mixture comprises the addition of a solvent to the mixture, thereby diluting the mixture and reducing its temperature. The amount of organic solvent to be added is dependent on the reaction temperature and the temperature at which reaction is effectively terminated. The addition of organic solvent to the reaction is effectively terminated. The addition of organic solvent to the reaction mixture is particularly preferred when the CCR resin is subsequently applied from solution.

A most preferred method for inhibiting the reaction comprises adding a material to the reaction mixture which effectively inhibits further reaction such as by deactivating the catalyst, or by interrupting the reaction mechanism, thereby inhibiting further reactions between the polyol and polyepoxide.

Strong inorganic and organic acids and the anhydrides and esters of said acids (including half esters and part esters) have been found to be particularly effective as reaction inhibitors. By the term "strong acid" it is meant an organic acid having a $PK_a$ value below about 4, preferably below about 2.5. Representative reaction inhibitors include inorganic acids such as hydrochloric acid, sulfuric acid and phosphoric acid; inorganic acid anhydrides such as phosphoric acid; anhydride ($P_{205}$); esters of inorganic acids such as dimethyl sulfate; the organic acids such as alkyl, aryl and aralkyl and substituted alkyl, aryl and aralkyl sulfonic acids such as $p$-toluene sulfonylic acid and phenyl sulfonylic acid and stronger organic carboxylic acids such as trichloroacetic acid and alkyl esters of said acids, such as the alkyl esters of
p-toluene sulfonic acid, e.g., methyl-p-toluene sulfonate, and ethyl-p-toluenesulfonate and methanesulfonic acid methylester. An example of an acid anhydride of a strong organic acid that can be employed herein is p-toluene sulfonic acid anhydride. Of the reaction inhibitors, the alkyl esters of sulfuric acid; the aryl or aralkyl sulfonic acids and the alkyl esters of said acids are preferably employed herein. Most preferably, an alkyl ester of para-toluene sulfonic acid, particularly methyl or ethyl-p-toluene sulfonic acid is employed as the reaction inhibitor herein.

The amounts of reaction inhibitor added to the reaction mixture are dependent on the specific inhibitor employed and the catalyst employed in preparing the CCR resin. In general, the inhibitor is added in an amount sufficient to overcome the catalytic activity of the catalyst. Preferably, at least about 0.9, more preferably at least about 2, equivalents of the inhibitor are added for each equivalent of the catalyst employed. Although the maximum amount of inhibitor added to the reaction mixture is dependent on the desired properties of the resin and the expense of adding excess inhibitor, the inhibitor is preferably added in an amount not exceeding about 5 equivalents for each equivalent of catalyst in the reaction mixture.

The reaction is terminated at a point such that the resulting CCR resin contains the desired amounts of epoxy groups and terminal hydroxyl groups. In this invention, the CCR resin will contain at least about 0.25 percent, by weight, of each of the epoxy and
terminal hydroxyl groups. By the term "epoxy group" it is meant a radical of the following structural formula:

\[
\begin{align*}
&\ce{H} \\
&\cdots \ce{C} \cdots \ce{CH} \\
&\ce{O} \\
&\ce{H} \quad \ce{H}
\end{align*}
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(V)

having an equivalent weight of 43 and by the term "terminal hydroxyl group" it is meant a terminal hydroxyl group having an equivalent weight of 17. For the purposes of this invention, the percent epoxy groups in the CCR resin reaction product is determined by the method described in Footnote (1) of Table I. The percent terminal phenolic hydroxyl groups is determined by the method described in Footnote 2 of Table I.

These weight percentages can also be viewed as the numbers of equivalents of the epoxy and hydroxyl groups per kilogram of the resin reaction product. It has been determined that 0.25 weight percent of the epoxy group is about 0.05 epoxy equivalents per kilogram resin produced. Similarly, 0.25 weight percent of the hydroxyl group is about 0.15 hydroxyl equivalents per kilogram resin produced.

The hydrolyzable chloride content of the CCR resin is generally less then about 1 and often less than about 0.5 percent based on the total weight of the epoxy resin reaction product. However, a hydrolyzable chloride content of up to about 5, preferably up to
about 2, weight percent based on the total weight of the epoxy resin reaction product can be tolerated. The amounts of hydrolyzable chloride are determined for the purpose of this invention by the method described in *The Handbook of Epoxy Resins* by H. Lee and K. Neville (supra) pages 4-29 and 4-30 (Table 4-23).

Conversion of the polyl and polyepoxide components is controlled such that the CCR resin contains the desired amounts of epoxy and hydroxyl groups. This conversion is dependent on the amount of polyl and epoxide employed. In general, it is desired that at least 10 percent and up to 90 or 95 percent of monomer type which is present in the lower amount (the deficient component) or, if the monomer types (components) are employed in equivalent amounts, of both components are reacted. Preferably, at least 35, more preferably at least 45, most preferably at least 55, and up to 95, more preferably up to 90, most preferably up to 85, percent of the deficient component are reacted.

The molecular weight (number average) of the CCR resin is dependent on the desired end-use application of the CCR resin and the physical and chemical properties required for said end use. Preferably, the CCR resins have a molecular weight of less than about 10,000. More preferably, the CCR resins will possess molecular weight of less than about 4000, preferably less than about 2000 and more than 300, preferably more than about 500.

In the practice of the present invention, the polyepoxide can be advanced with a polyl and, optionally, a polyacid to completion (thereby forming a
resin having either only epoxy groups or terminal hydroxyl groups depending on which reactant is employed in excess) in one reaction step and thereafter reacted with a polyol or a polyepoxide component to form the CCR resin. However, more preferably, the polyepoxide such as the diglycidyl ether of bisphenol A is reacted, in a one step reaction, with the polyol to form the desired CCR resin.

Although the amount of epoxy groups and terminal hydroxyl groups most advantageously contained by the CCR resin and hence by the improved resin according to the present invention is dependent on the desired properties of the final resin product, e.g., its solution viscosity, it has been found desirable for the final resin produced according to the invention to have a total of at least 0.15 equivalents of terminal phenolic hydroxyl groups per kilogram resin and at least 0.05 equivalents of epoxy groups and epoxy derived groups per kilogram resin, (eq/kg) with at least a portion being the epoxy-derived groups. Of course a corresponding number of equivalents of the hydroxyl and epoxy groups are necessary in the controlled conversion resin from which the present resins are prepared. It has been found that the number of epoxy groups in the controlled conversion resins suitable for use according to the present invention is preferably from 0.058 to 2 equivalents per kilogram resin and more preferably from 0.1 to 1 equivalent, prior to conversion to the epoxy-derived group, while the preferred number of terminal phenolic hydroxyl equivalents is from 0.15 to 5.88, more preferably 1 to 3, per kilogram resin. Most preferably the resins contain from 0.2 to 0.8 eq/kg of epoxy groups prior to
conversion of any of the epoxy groups to epoxy-derived groups and 1.5 to 2.5 eq/kg terminal phenolic hydroxyl groups.

It was found not only that the above ranges of hydroxyl group and epoxy group concentrations were necessary in the controlled conversion resins to produce epoxy resins especially good for solution coating formulations, but surprisingly that the conversion of at least a portion of the epoxy groups into epoxy-derived groups further improved the curing rate of these resin formulations. Preferably, the number of terminal phenolic hydroxyl groups is not substantially changed. It was found that when the epoxy groups of these controlled conversion resins were further reacted to form epoxy-derived groups such as alpha-glycol or phosphate ester groups, curing times are substantially reduced while good resin and coating properties are maintained.

In general, the epoxy groups of the controlled conversion resin can be converted to any sort of epoxy-derived functional group that will not detrimentally affect the curing reaction. Although the present invention is in no way limited by such theory, it is believed that a hydrolysis reaction of the epoxy group with added water forms alpha-glycols and is a way to conveniently convert the epoxy groups to suitable epoxy-derived groups. In this regard, the number of equivalents of epoxy groups will determine the amount of water or other reactant necessary to form the alpha-glycol and possibly other types of epoxy-derived groups. In general, water is used in excess amounts of
from 0.5 to 20 weight percent based on the total resin weight, preferably 1 to 10 weight percent.

Reaction of the controlled conversion resins with water and acid can also be employed to convert the epoxy groups. It is theorized that this is a conversion of the epoxy groups to alpha glycols and acid esters and possibly other types of groups derived from the epoxy groups but the present invention is not to be limited by this theory. Water and acid are used generally in amounts of 0.3 to 10 weight percent water and 0.1 to 5 weight percent acid, these weight percentages based on the total weight of the resin to which the water and acid are added. More preferably the respective weight percentages of water and acid are 0.5 to 3 weight percent and 0.2 to 2 weight percent.

In a preferred method of practicing the present invention the epoxy groups of the controlled conversion resin are reacted with water and a phosphorous-containing acid. Although not limiting the invention, the theory is that there is conversion of the epoxy groups into a mixture of epoxy-derived groups comprising at least alpha glycol groups and phosphorous-containing acid ester groups and possibly other groups. In this embodiment, the amounts of water and phosphorous-containing acid (preferably phosphoric acid) are balanced to maximize the mono-esters and minimize the tri-esters. It has been found generally that when the phosphorous-containing acid is used in this way with a controlled conversion resin it should be added in amounts of from 0.1 to 3 weight percent based on the resin weight, preferably from 0.2 to 1.5 weight percent while the water used in conjunction should be added in amounts of from 0.2 to 10 weight
percent based on the resin weight, preferably from 0.5 to 3 weight percent.

In another preferred embodiment of the present invention, in one step amounts of water and acid, and preferably a phosphorous-containing acid, are employed as a reaction inhibitor in preparing the controlled conversion resins, in excess of amounts taught to inhibit the polyol polyepoxide reaction, which excess amount is then able to react with the epoxy groups of the controlled conversion resin to form the epoxy-derived groups, most preferably, the above-described mixture of such groups comprising alpha-glycols and phosphorous-containing acid esters. When used in this fashion to both inhibit the reaction and convert the epoxy groups to epoxy-derived groups, the acid is used in amounts of from 0.1 to 3 weight percent based on the weight of resin, preferably from 0.2 to 1.5 weight percent.

It has been found that at least 30 percent of the epoxy groups of a controlled conversion resin need to be converted to epoxy-derived groups in order to improve the curing rate, preferably more than 50 percent and most preferably substantially all the epoxy groups are converted. Although containing substantially no epoxy groups, such resins are referred to herein as epoxy resins in view of their origin. Of course when the reaction is inhibited and the epoxy groups are converted in a single step and/or by a single reactant such as phosphoric acid, there is not necessarily isolated a controlled conversion resin having a specific epoxy group content. In these types of situations, within the scope of the present invention, the reduced number epoxy groups remaining in
the final resin product (if any) and the presence of
the epoxy-derived groups will be indicative of the
practice of the present invention and will produce the
improved resins thereof.

Upon preparation of the improved CCR resin, it
can be formulated into a number of different
compositions for use in a variety of end-use
applications. Preferably, following preparation of the
improved CCR resin, it can be dissolved in an organic
liquid for subsequent application. Suitable organic
liquids for preparing the organic liquid solution of
the resin are dependent on the particular resin and the
amounts of terminal -OH, epoxy and epoxy-derived
groups in the resin. In general, alcohols, such as n-
butanol, glycol ethers such as propylene glycol
monomethyl ether and esters thereof, ketones, aliphatic
or aromatic hydrocarbons such as xylene and chlorinated
aliphatic and aromatic hydrocarbons are preferred.

In preparing an organic liquid solution of the
resin, it is generally desirable to employ a hardener
which is also soluble in the organic liquid. Such
hardeners are well-known in the art and reference is
made thereto for the purposes of this invention.
Representative hardeners include phenolic resole resins
such as the reaction product of phenol with an excess
of formaldehyde and other hydroxymethyl-containing
benzene derivatives and alkylated derivatives thereof
and amine-aldehyde condensates, commonly referred to as
"aminoplast" or "aminoplastics" which are the
condensation products of an aldehyde with an amine such
as melamine, urea and benzoquinamine and the alkylated
derivatives thereof.
The amount of the hardener most advantageously employed is dependent on a variety of factors including the end-use application for the organic liquid solution and the desired physical and chemical properties of said end-use application. Preferably, from about 1 to about 50 weight percent of the hardener are employed based on the total weight of the improved CCR resin and hardener.

In addition, it is possible, though not essential, to add a small amount of an inorganic acid to the organic liquid solution as a catalyst for the reaction of the improved CCR resin with the hardener. In general, the inorganic acid is preferably phosphoric acid and is used in an amount from about 0.1 to about 5 weight percent based on the total weight of the organic liquid solution. Especially if epoxy groups of the resin have been reacted to phosphate esters, this hardening catalyst may not be needed.

The solids concentration at which the organic liquid solution is prepared is dependent on various factors including the desired viscosity of the resulting solution. In general, the organic liquid solution is formulated such that the solids content is as high as possible while maintaining a sufficiently low viscosity for effective application. Since the improved CCR resins exhibit a lower solution viscosity than conventional resins which would possess equivalent cured properties, the organic liquid solution of the resin can generally be prepared at higher solids concentrations than an organic liquid solution of a conventional resin. For example, a resin useful in coating applications may advantageously be formulated as an organic liquid solution which comprises at least
30 percent of the resin and any hardener employed based on the total weight of the organic liquid solution. More preferably, the liquid solution contains at least 40 percent, preferably from 50 weight percent or more of the resin and hardener.

The following examples are set forth to illustrate the invention and should not be construed to limit its scope. In the examples, all, parts and percentages are by weight unless otherwise specified.

Examples:

A 6 liter stainless steel pressure reactor was equipped with an agitator, a heating jacket receiving a circulation of oil from an oil thermostat and a nitrogen line for creating an inert nitrogen atmosphere at pressures from 0 to 6 bars. A one liter feeding tank was connected with a steel piping to the reactor which could be pressurized with nitrogen for feeding liquids under pressure into the reactor.

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<th>Components</th>
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<td>Polyepoxide</td>
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<td>Polyol</td>
<td>Bisphenol A</td>
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<td>Catalyst</td>
<td>Ethyltriphenyl phosphonium acetate monacetic acid complex (70 weight % solution in methanol)</td>
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<td>Reaction inhibitor</td>
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</table>

Example 1
2707 grams (15.0 equivalents) of polyepoxide and 2802 grams (24.6 equivalents) of polyol were added to the reactor. The components were mixed together and heated to 90°C to dissolve the polyol in the polyepoxide. Then 2.11 grams (g) of catalyst were added to the reaction mixture. The reaction mixture was slowly heated up with agitation and under a nitrogen blanket and maintained at 140°C during approximately 2 hours until the analysis of a sample indicated an epoxy content of 0.41 eq/kg and a phenolic hydroxyl content of 2.0 eq/kg. At that moment 1.94 g of reaction inhibitor was introduced into the reactor and the mixture stirred for one additional 1/2 hours. The analysis of a sample taken from the reactor indicated that the CCR resin intermediate contained 0.36 eq/kg epoxy end groups and 1.94 eq/kg phenolic hydroxyl groups.

The reactor was then closed and 135.9 g of a phosphoric acid solution in water containing 25.9 g of commercial 85 percent by weight orthophosphoric acid (0.4% H₃PO₄ on total resin) and 110 g of water (2 percent H₂O based on total resin) were introduced into the reactor from the feeding tank with the help of a nitrogen pressure. The nitrogen over-pressure was increased to 5 bars. The temperature and the pressure were maintained at 135°C and 5 bars respectively for a reaction time of 2 hours.

The pressure was then reduced and the excess water evacuated from the resin under reduced pressure for 30 minutes at 135°C. The resin was then drained from the reactor through a bottom valve and solidified.
The properties of the resin derived from the CCR resin are summarized in Table I.

Example 2

A resin derived from a CCR resin was prepared using the techniques of Example 1 except that 1969 g of polyepoxide (10.9 equivalents) and 2038 g of polyol (17.9 equivalents), 1.54 g of catalyst and 1.41 g of reaction inhibitor were employed. The amounts of water and phosphoric acid used to react with the CCR resin were respectively 2.0 weight percent and 0.8 weight percent based on the total resin weight. The properties of this resin are summarized in Table I below.

Example 3

Example 2 was repeated except that the amounts of water and phosphoric acid used to react with the CCR resin were respectively 0.7 and 1.0 weight percent based on the total weight of the resin. The results are summarized in Table I below.

Example 4

Example 2 was repeated except that the reaction inhibitor was not used. Instead a phosphoric acid solution in water was directly charged to the reactor. The amount of water and phosphoric acid used being 1.0 weight percent of each based on total resin weight. The results of the resin analysis and evaluation are summarized in Table I.

This example demonstrates that phosphoric acid can be used at the same time as reaction inhibitor for
the CCR resin and as reactant with the epoxy groups to produce the improved resin of this invention.

Example 5

A CCR derived resin was prepared using the technique of Example 1 except that 1969 g of polyepoxide (10.9 equivalents), 2039 g of polyol (17.9 equivalents) and 1.54 g of catalyst were employed. 141 g of the reaction inhibitor was added to the reactor at a slightly higher epoxy content so that the CCR resin prepared contained 0.44 eq/kg of epoxy end groups and 2.3 eq/kg of phenolic hydroxyl end groups. This point was reached after stirring and heating the mixture at 143°C for 1 hour and 55 minutes. The reaction mixture containing the inhibitor was then stirred at 140°C for 30 minutes. 240 g of water (6 weight percent based on total resin) was then transferred from the feeding tank into the reactor using a 5 bars nitrogen pressure.

The reaction mixture was then stirred at 140°C under 5 bars overpressure during 4 hours. The pressure was then slowly released and the excess water evacuated from the reactor under a nitrogen flow first, followed by slightly reduced pressure, the temperature being maintained at 140°C. The resin derived from the CCR resin was then drained from the reactor and allowed to cool and solidify. The analysis of the remaining epoxy groups demonstrated that the residual epoxy groups from the CCR resin were partly hydrolyzed. The final resin contained 0.28 equivalents epoxy and 2.2 equivalents phenolic OH groups per kg resin. The results of the resin analysis and evaluation are summarized in Table I.
Table I

<table>
<thead>
<tr>
<th>Examples</th>
<th>1</th>
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<th>3</th>
<th>4</th>
<th>5</th>
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<td>Polyol (g)</td>
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<td>Catalyst (g)</td>
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<td>1.41</td>
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CCR intermediate

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<tr>
<th></th>
<th>eq. epoxy/kg(^1)</th>
<th>eq. OH/kg(^2)</th>
<th>wt.% H(_3)PO(_4)</th>
<th>wt.% water</th>
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<tr>
<td></td>
<td>0.36</td>
<td>2.09</td>
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CCR derived resin

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<th>eq. OH/kg(^2)</th>
<th>eq. epoxy-derived groups/kg(^5)</th>
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<tr>
<td></td>
<td>0.02</td>
<td>1.93</td>
<td>0.34</td>
</tr>
<tr>
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<td>0.02</td>
<td>2.09</td>
<td>0.34</td>
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<tr>
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<td>2.0</td>
<td>0.34</td>
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<td></td>
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<td>2.2</td>
<td>0.16</td>
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150°C Melt

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<td>Softening Point(^4)</td>
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<td>104.0</td>
<td>93</td>
</tr>
</tbody>
</table>

Footnotes - Table 1

\(^1\)Analysis of Epoxide Groups

The weight percent epoxide groups in the CCR resin was determined by preparing
(a) a perchloric acid solution by (1) placing 250 ml of glacial acetic acid into a one liter flask, (2) adding and mixing 13 ml of a 60 percent aqueous solution of perchloric acid into the flask, (3) adding 50 ml of acetic anhydride to the flask, (4) filling the flask to 1 liter with glacial acetic acid and (5) allowing the mixture to age for 8 hours to complete reaction between acetic anhydride and water. The perchloric acid solution is standardized using potassium acid phthalate (0.4 g of potassium acid phthalate in 50 ml of glacial acetic acid) or with the crystalline diglycidyl ether of bisphenol-A;
(b) a tetraethyl ammonium bromide TEAB) solution by dissolving, at room temperature, with agitation, 100 g of TEAB in 400 ml of glacial acetic acid;
(c) a 0.1 percent solution of crystal violet indicator in glacial acetic acid.

A solution of the CCR resin was prepared using an amount of the CCR resin which contains 0.001 to 0.002 equivalent of epoxy groups by initially weighing the amount of the sample (nearest milligram) into a 2-ounce disposable glass bottle. Thereafter, 10 ml of methylchloride was added to the bottle. A clean magnetic stirrer was used to dissolve the sample of CCR resin and throughout titration. Subsequently, 10 ml of the TEAB solution was added to the CCR resin solution and then 6-8 drops of crystal violet indicator were added. It was then titrated with 0.1 N-perchloric acid.
to endpoint which is a sharp color change from blue to green and which is stable for 30 seconds.

The weight percent epoxide groups was then calculated using the formula:

\[
\%E = \frac{F \times B \times 4.3}{W}
\]

The equivalents epoxide groups per kilogram resin was calculated using the formula

\[
\text{eq/kg} = \frac{\%E \times 10}{43}
\]

wherein the \(\%E\) = percent, by weight, of epoxy groups in the CCR resin.

- \(F\) = normality of perchloric acid solution
- \(B\) = the volume (in millimeters) of the perchloric acid solution used in the titration of the endpoint
- \(W\) = weight (in grams) of epoxy resin sample.

2Analysis of Terminal Phenolic Hydroxyl Groups

The residual phenolic hydroxyl (weight percent phenolic hydroxyl groups in the CCR resin) was determined by dissolving the CCR resin in a basic
medium such as pyridine and titrating to endpoint with a strong base such as tetrabutyl ammonium hydroxide or sodium methylate. In this example, the percent hydroxyl was determined by initially placing 75 ml of pyridine in a 250 ml beaker fitted with a rubber stopper having two holes – one hole for a nitrogen inlet and the other hole for the titration buret – and containing a magnetic stirrer. While agitating, the inside of the beaker was purged with nitrogen for 2 to 3 minutes. An Azoviolet indicator, as a saturated solution in benzene, was then added to the pyridine until the solution became a good straw yellow color. This mixture was titrated with 0.1 N-tetrabutyl ammonium hydroxide to a blue endpoint which normally requires only a few drops. The nitrogen purge was continued for an additional 2 to 3 minutes after this time.

A sample of the CCR resin containing one milliequivalent or less of phenolic hydroxyl groups was dissolved into the pre-titrated pyridine. The nitrogen blanket was maintained and the CCR resin allowed to dissolve. The solution was subsequently titrated using a 0.1 N-tetrabutylammonium hydroxide to a blue endpoint. For accurate determination, the tetrabutylammonium hydroxide (TBAH) solution should contain no water.

The weight percent hydroxide groups in the CCR resin were determined using the following formula:
$$D = \frac{1.7 \times N \times (E-F)}{U}$$

wherein $D =$ weight percent phenolic \(-\text{OH}\) groups in the CCR resin

$N =$ the normality of TBAH solution

$E =$ the total volume of the TBAH titrant used in ml

$F =$ the volume of the TBAH titrant in ml used in the pre-titration

$U =$ weight of the sample of the CCR resin in grams

The equivalents phenolic hydroxyl groups per kilogram resin is derived from the weight percent $D$ using the following formula:

$$\text{eq. OH/kg} = \frac{D \times 10}{17}$$

3Melt viscosity is defined as the viscosity of the molten resin at the specified temperature as measured using an ICI cone and plate viscometer.

4Softening point is defined as the temperature at which the epoxy resin suspended in a cup with a 6.35 mm hole in the bottom flows downward at a distance of 19 mm as
the sample is heated at a liner rate in air. It was measured using ASTM test method designated D-3104-77 using a Mettler softening point apparatus model FP5/53. Epoxy-derived groups.

The equivalents of epoxy-derived groups per kilogram resin was calculated as the difference between the number of equivalents of epoxy groups in the CCR intermediate and the number of epoxy groups found in the final resin product, where there was a reaction that reacted the epoxy groups of a CCR resin.

Comparative Examples

The same reactor equipment as described for the Examples 1-5 was employed as needed. These examples and the results are summarized below in Table 2.

Comparative Example A

2379 g (13.2 equivalents) of polyepoxide and 2121 g (18.6 equivalents) of polyl were charged to the reactor under a nitrogen atmosphere. The components were mixed together and heated to 90°C to dissolve the polyl in the polyepoxide. Then 1.68 g of catalyst were added to the reaction mixture. The reaction mixture was then heated to 140°C and maintained at this temperature for 2 hours and 10 minutes. At the end of this time 1.55 g of reaction inhibitor was added to the reaction mixture. The reaction mixture containing the reaction inhibitor was subsequently stirred and maintained at 140°C for one hour. At this time the reaction product was drained from the reactor and allowed to cool and solidify.
The CCR resin thus prepared contained 0.61 equivalents epoxide groups per kg resin and 1.75 equivalents phenolic groups per kg resin.

Comparative Example B

A CCR resin was prepared using the techniques of Comparative Example A except that 2375 g (13.2 equivalents) of polyepoxide, 2625 g (23.0 eq.) of polylol and 1.85 g of catalyst were employed. The reaction mixture was stirred and maintained at 135°C for two hours and then at 140°C for 1 3/4 hours. At this time, 1.70 g of reaction inhibitor was added to the reaction mixture. The reaction mixture containing the reaction inhibitor was stirred and maintained at 140°C for one hour. The resin was then drained from the reactor and allowed to cool and solidify. The resin was analyzed and found to contain 0.30 equivalents epoxy groups and 2.15 equivalent phenolic hydroxyl groups per kg resin.

Comparative Example C

A fully converted resin was prepared by admixing in the reactor under nitrogen sparge 2357 g (13.1 equivalents) of polyepoxide and 2642 g (23.2 equivalents) of polylol. The mixture was heated to 90°C and 2.5 g of catalyst was added to the reaction mixture.

The reactor content was then heated to 150°C. The exothermic reaction caused the temperature to increase to 175°C. The reaction mixture was stirred and maintained at 170°C for 2 hours. The resin was then drained from the reactor and allowed to cool and solidify. This resin was found to contain 1.94
equivalents phenolic hydroxyl end groups and virtually no epoxy groups (less than 0.02 equivalents per kg).

Comparative Example D

A fully converted resin was prepared using the techniques of comparative Example C except that 2607 g (14.5 equivalents) of polyepoxide, 1392 g (12.2 equivalents) of polyl and 3.12 g of catalyst were employed. The exotherm peak temperature reached 205°C for this resin. After analysis this typical high molecular weight epoxy resin was found to contain 0.58 equivalents epoxy groups (EEW = 1730) and less than 0.05 equivalent phenolic hydroxyl group per kg resin.

Table 2 summarizes the compositions and analytical results of comparative examples A, B, C, and D.
Table 2

<table>
<thead>
<tr>
<th></th>
<th>CCR's 0.05</th>
<th>Fully Converted Resins</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Polyepoxide (g)</td>
<td>2379</td>
<td>2375</td>
</tr>
<tr>
<td>Polyol (G)</td>
<td>2121</td>
<td>2625</td>
</tr>
<tr>
<td>Catalyst (g)</td>
<td>1.68</td>
<td>1.85</td>
</tr>
<tr>
<td>Inhibitor (g)</td>
<td>1.55</td>
<td>1.70</td>
</tr>
<tr>
<td>Eq. Epoxy/kg(^1)</td>
<td>0.61</td>
<td>0.30</td>
</tr>
<tr>
<td>Eq. Epoxy-derived groups/kg(^5)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Eq. OH/kg(^2)</td>
<td>1.75</td>
<td>2.15</td>
</tr>
<tr>
<td>150C melt viscosity(^3) (Pa·s)</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Softening point(^4) (°C)</td>
<td>93.6</td>
<td>102</td>
</tr>
</tbody>
</table>

Comparative Examples

Footnotes Table 2 same as for Table 1

Coating Compositions

Coating compositions have been prepared with all resins of Examples 1 to 5 and comparative Examples A to D following the general description below:

Each coating composition was prepared by blending 36.8 parts of the resins with 22.5 parts of a phenolic resin hardener sold by Hoechst under the tradename Phenodur® PR 612 (70 percent solution in butanol), a mixture of organic liquids comprising propylene glycol monomethyl ether: propylene glycol monomethyl ether acetate: xylene in a ratio of 2:1:1, respectively sufficient to reach a final viscosity at
25°C of 250 mPa-s (0.250 Pa-s), 0.53 parts of a 25 weight percent solution of phosphoric curing catalyst in glycol ether and 0.53 parts of silicon flow agent. The solids content of each formulation was recorded.

The coating compositions were applied to a tin coated steel substrate, the organic solvent evaporated and the resins cured in an oven at 200°C for various lengths of time (5, 10 and 20 minutes). The coating properties were evaluated for the speed of cure measured by the number of acetone double rubs resistance and the flexibility measured by the percent wedge bend flexibility. Both of these test methods are comparative tests for coating properties well known in the coating industry: the higher the acetone double rubs (ADR) the better the cure, the higher the percent wedge bend flexibility (0-100 percent) the better the flexibility. These methods are described below.

**Acetone Double Rubs**

A small cotton wool pad is soaked with acetone, applied to the coating and rubbed back and forth over the same area with even pressure until the continuity of the coating is destroyed. The number of "double rubs" necessary for this is noted.

**Wedge Bend**

Using a Gardner I-G-1125 Bend and Impact Tester, a coated substrate of width 10 cm is bent over a 5 mm mandrel with the lacquered side outwards. This sample is placed between a "hammer" and anvil such that a differential radius of curvature is produced along the length of the sample bend (10 cm), ranging from a very sharp bend (0 mm radius of curvature) to a rounded
profile (1.59 mm radius curvature). The length of the continuous coating, starting at end with the rounded profile end and going in the direction toward the sharply bent end, along the bend, in centimeters, divided by 10 (the edge length) gives a percentage indicating the flexibility of the film. In some cases the coating was too brittle and there were discontinuities along the entire length of the bend. This is indicated by the word "brittle".

Storage Stability

The storage stability of the formulation was measured by the viscosity increase after 8 weeks storage at 40°C. The formulations and the measured coating properties are recorded in Table 3.
<table>
<thead>
<tr>
<th>Formulations</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent solids for 0.250 Pa·s viscosity</td>
<td>51</td>
<td>51</td>
<td>51</td>
<td>51</td>
<td>51</td>
<td>54</td>
<td>54</td>
<td>51</td>
<td>42</td>
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<tr>
<td>Viscosity after 8 weeks storage at 40°C, Pa·s</td>
<td>0.270</td>
<td>0.260</td>
<td>0.290</td>
<td>0.280</td>
<td>N.D.</td>
<td>0.390</td>
<td>0.360</td>
<td>0.2700</td>
<td>0.480</td>
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<td>5 min. cure/200°C ADR</td>
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<td>5</td>
<td>10</td>
<td>10</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<tr>
<td>% wedge bend</td>
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<td>75</td>
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<tr>
<td>10 min. cure/200°C ADR</td>
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<td>30</td>
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<td>20 min. cure/200°C ADR</td>
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<tr>
<td>% wedge bend</td>
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<td>65</td>
<td>73</td>
<td>46</td>
<td>brittle</td>
<td>83</td>
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The data from Table 3 demonstrate that the resins of this invention show surprisingly improved combinations of cure speed and storage stability compared to the CCR resin of comparative Example A and B. The resin from comparative Example C, containing only phenolic end groups and no epoxy groups or groups derived from epoxy groups does not develop adequate flexibility at all, even after 20 minutes cure.

The resin of comparative Example D is an example of an epoxy resin of the type commonly used for interior can coatings. It develops the needed properties after 10 minutes cure as compared to 5 minutes curing time for the resins of this invention. In addition, resin D can be formulated at a maximum solids content of 42 percent as compared to 51 percent solids for the resins of this invention.

Furthermore, it has been found that the resins of Examples 2, 3 and 4 could be formulated into the same coating formulations omitting the 0.53 parts of added curing catalyst solution and develop same properties after the same curing times.

On the contrary a four fold increase of the curing catalyst added to the formulation did not improve the coating properties for comparative Examples A, B, C, and D.
1. An epoxy resin comprising the reaction product of a polyepoxide and a polyol wherein the reaction product contains,
   (a) terminal phenolic hydroxyl groups in an amount of at least 0.15 equivalents per kilogram resin (eq/kg),
   (b) groups derived from epoxy groups, and optionally
   (c) epoxy groups,
   the total amount of groups (b), and, if present (c) in the resin being at least 0.05 equivalents, per kilogram of resin.

2. An epoxy resin as claimed in Claim 1, wherein the total amount of groups (b) and, if present (c) groups in the resin is from 0.058 to 2 equivalents per kilogram of resin.

3. An epoxy resin as claimed in Claim 2 wherein the resin contains substantially no epoxy groups.
4. An epoxy resin as claimed in any one of the preceding claims wherein the resin contains from 1 to 3 terminal phenolic hydroxyl groups equivalents per kilogram of resin.

5. A process for preparing an epoxy resin which method comprises reacting a polyeopoxide with a polyl in the presence of a catalyst for the reaction of an epoxy group with a hydroxyl group and terminating the reaction at a point when the reaction product contains at least 0.05 equivalents epoxy groups per kilogram of resin and 0.15 equivalents terminal phenolic hydroxyl groups per kilogram of resin, then reacting at least a portion of the epoxy groups to form epoxy-derived groups.

6. A process as claimed in Claim 5, wherein the epoxy groups are reacted with water.

7. A process as claimed in Claim 6, wherein the epoxy groups are reacted with water and acid.

8. A process as claimed in Claim 7, wherein the epoxy groups are reacted with water and phosphoric acid.

9. A process as claimed in Claim 5, wherein the reaction of the polyeopoxide and polyl is terminated and the epoxy groups are reacted with phosphoric acid in a single process step.

10. A coating composition which comprises an epoxy resin as claimed in any one of Claims 1 to 4 or prepared by a process as claimed in any one of Claims 5 to 9.
### INTERNATIONAL SEARCH REPORT

**International Application No**

PCT/US 87/00344

### I. CLASSIFICATION OF SUBJECT MATTER

(If several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

**IPC**

C 08 G 59/06; C 08 G 59/14

### II. FIELDS SEARCHED

**Classification System**

Minimum Documentation Searched

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Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched

### III. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of Document, with indication, where appropriate, of the relevant passages</th>
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<td>A</td>
<td>GB, A, 2149409 (ASAHI DENKA) 12 June 1985 see page 1, line 18 - page 2, line 43; claim 1</td>
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<td>A</td>
<td>WO, A, 83/00045 (DOW) 6 January 1983 see page 9, line 10 - page 10, line 17; page 11, line 22 - page 12, line 2; claim 1</td>
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<td>WO, A, 86/01216 (DOW) 27 February 1986 see the whole document</td>
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* Special categories of cited documents:
  - "A" document defining the general state of the art which is not considered to be of particular relevance
  - "E" earlier document but published on or after the international filing date
  - "L" document which may throw doubt on generic claims or which is cited to establish the publication date of another document or other special reasons (as specified)
  - "O" document relating to an oral disclosure, use, exhibition or other means
  - "P" document published prior to the international filing date but later than the priority date claimed
  - "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  - "X" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
  - "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
  - "Z" document member of the same patent family

### IV. CERTIFICATION

Date of the Actual Completion of the International Search: 15th May 1987

Date of Mailing of the International Search Report: 22 Jun 1987

International Searching Authority: EUROPEAN PATENT OFFICE

Signature of Authorized Officer: [Signature]

Form PCT/ISA/210 (second sheet) (January 1985)
ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 87/00344 (SA 16296)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 10/06/87.

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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